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Organic Calcium Co-ordinate Compounds

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The subject of organometallic ring compounds, or chelates, is dealt with comprehensively by Diehl (Ref. 1) who, using the terminology of Morgan, classifies the compounds as bidentate, tridentate, etc., according to the number of links or "teeth," and further differentiates as to whether the bonds are primary (from acidic groups), secondary (co-ordinate), or a mixture of both. Calcium falls among the elements of his system which have a co-ordination number of six and a primary valence of two.

Calcium does not readily form co-ordinate compounds, so the literature on this subject is rather meager. The formation of insoluble chelates, such as the picrolonate, is important analytically but does not directly concern the present work, which is confined to soluble, sparsely ionized compounds. Patents have been issued on the preparation and use of amino-polyacetic acids (Ref. 2), while Pfeiffer has prepared their calcium derivatives (Ref. 3); and the investigations of Schwarzenbach and his co-workers have done much to measure and clarify the action of these acids in reducing the availability of calcium ions (Refs. 4-6). The comprehensive work of Hein (Ref. 7) on co-ordination compounds also includes reference to the amino-polyacetic acid compounds and mentions a few other co-ordination complexes, but emphasizes the inertness of the calcium ion to complex formation.

The data presented here were gathered in a study of the prevention of calcium precipitates in a photographic developer. However, the results of this research are of more interest to the organic chemist than to the photographer, since they relate the structure of the compound with its ability to form un-ionized complexes. This ability was measured by a type of titration which determined the net quantity of calcium necessary to produce a visible precipitate of calcium sulfite under fixed equilibrium conditions. They apply to a moderately alkaline solution of pH = 9.8. These measurements of the reduction in the concentration of calcium ions appear to be in agreement, where data are available, with those made by Schwarzenbach and his co-workers with an entirely different method.

Several aspects of the effect of the constitution of the agent upon its ability to form calcium complexes may be deduced from the magnitude of the sequestering values entered in Table II. The probable nature of some of these chelates is shown in Table I. Some of these structures appear in the literature, while others seem reasonably analogous, and bonding angles and distances of selected structures have been checked. However, no attempt has been made to isolate the complexes.

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The Influence of Structure on Complex Formation

1. Primary and secondary groups. The successful sequestering agent must contain both a primary group, that is, one yielding a covalent bond such as carboxy or nitroso, and a group yielding a secondary or co-ordinate link such as hydroxy or amino. Compounds in which both groups are of the same type have proved weak or unsuccessful (see Table II, Nos. 30, 31, 32). There seems to be little distinction between the action of the phenolic groups of gallic acid, No. 13, and the hydroxy groups of gluconic acid, No. 10.

2. Size of the ring. All the potent compounds examined have the functional groups placed alpha to each other so as to form 5-membered rings with the calcium atom, although weak sequestering is obtained with 6-membered rings. Compare Nos. 9 and 17, but note the supplementary action of the 6-membered ring when comparing No. 12 with No. 14 (Table II).

3. Multiple chelation. Polydentate chelates, in which more than one ring is formed, show greatly increased sequestering action. This effect has been described previously for amino-carboxylic acids but also applies to hydroxy acids. Some examples of the structures probably formed are shown in Table I, and the sequestering values are given in Table II. The numbering of the compounds is the same in the two tables.

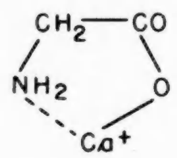
The power of the ethylenediamine tetracetic acid complex to repress ionization, and the high stability of the sexadentate chelate formed are shown by both experimental and practical evidence, and ethylenediamine tetracetic acid enjoys considerable commercial importance. Nitrolo triacetic acid, No. 2, has also enjoyed commercial importance but forms less stable complexes.

There is no reason why chelation in the oxygen series could not be extended as far as in the amino series except for the difficulties of synthesis, and the structure of one possible sexadentate chelate, ethylene *bis*-tartronic acid, is sketched as No. 33 in Table I.

4. Aromatic compounds. The functional groups may be attached to a benzene ring, as in Nos. 13 and 22. In Compound 16, on the other hand, the benzene ring has been substituted in the aliphatic compound without materially changing its sequestering ability.

5. Heterocyclics. The functional groups may form part of a heterocyclic ring, as in Nos. 20 and 21, where the furane ring is used (these are weaker than Nos. 14 and 7). The dicarboxyimidazole, No. 18, forms an analogue to No. 3, while No. 19 appears to be unique.

TABLE I



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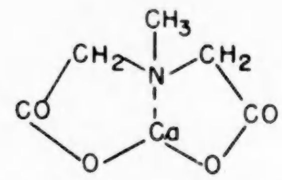

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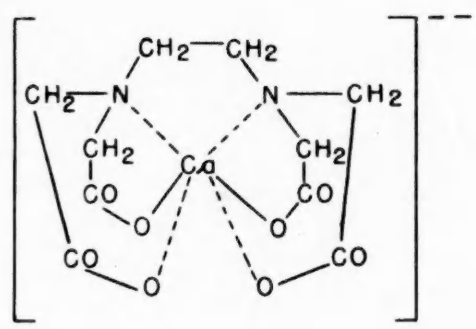

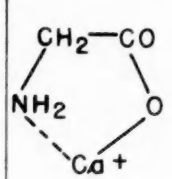

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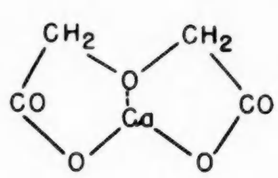

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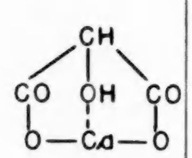

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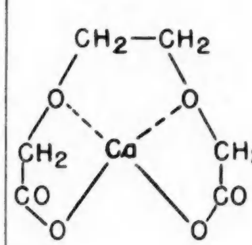

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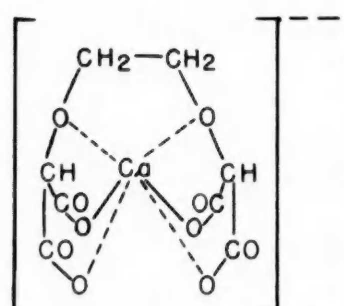

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TABLE II. Calcium-Sequestering Power of Various Addends in a Sulfite–Borate Photographic Developer

No.	Compound	Sequestering (Millimoles Calcium Chloride)	
		Per Mole	Per Acid Group
	Amino-Carboxylic Acids		
1	Ethylenediamine tetracetic acid $(HOOCCH_2)_2NCH_2CH_2N$-$(CH_2COOH)_2$	1000	250
2	Triglycin (nitrolo triacetic acid) $N(CH_2COOH)_3$	700	240
3	Methylamino diacetic acid $CH_3N(CH_2COOH)_2$	180	90
4	Aspartic acid $HOOCCH_2CH(NH_2)COOH$	35	18
5	Glycin H_2NCH_2COOH	4	4
	Oxy-Carboxylic Acids		
6	Tartronic acid $(HOOC)_2CHOH$	200	100
7	Diglycolic acid $(HOOCCH_2)_2O$	170	85
8	Ethylene *bis*-glycolic acid $HOOCCH_2OCH_2CH_2$-OCH_2COOH	130	65
9	Pyruvic acid $CH_3COCOOH$	60	60
10	Gluconic acid $HOOC(CHOH)_5H$	90	90
11	Quinone tetracarboxylic acid $C_6O_2(COOH)_4$	100	25
12	Malic acid $HOOCCHOHCH_2COOH$	35	18
13	Gallic acid 3,4,5-$(HO)_3C_6H_2COOH$	40	40
14	Glycolic acid $HOCH_2COOH$	6	6
15	Lactic acid $HOCH(CH_3)COOH$	6	6
16	Mandelic acid $HOCH(C_6H_5)COOH$	10	10
17	Levulinic acid $CH_3COCH_2CH_2COOH$	5	5

No.	Compound	Sequestering (Millimoles Calcium Chloride)	
		Per Mole	Per Acid Group
	Heterocyclics		
18	Imidazole-4,5-dicarboxylic acid $HOOCC=C(COOH)N=CHNH$	170	85
19	Alloxan $NHCONHCOCOCO$	75	—
20	Dehydromucic acid $HOOCCOC(COOH)CH=CH$	14	7
21	Furoic acid $HC=CHCH=C(COOH)O$	2	—
	Nitro and Nitroso		
22	Nitrosoresorcinol 1-NOC_6H_3-2,4-$(OH)_2$	320	320
23	Picric acid 2,4,6-$(NO_2)_3C_6H_2OH$	80	27
	Diazo		
24	Diazomalonic acid $HOOCCH(N=N)COOH$	140	70
	Unsaturates		
25	Maleic acid $HOOCCH=CHCOOH$	20	10
26	Acetylene dicarboxylic acid $HOOCC\equiv CCOOH$	20	10
	Mercapto-Carboxylic		
27	Quinone tetrathioglycolic acid $C_6O_2(SCH_2COOH)_4$	140	35
28	Thioglycolic acid $HSCH_2COOH$	0.5	0.5
29	Thiodiglycolic acid $S(CH_2COOH)_2$	3	1.5
	Lack Sequestering Action		
30	Pyromelitic acid C_6H_2-1,2,3,4-$(COOH)_4$		
31	Ethylenediamine tetraglycol $(HOCH_2CH_2)_2NCH_2CH_2N$-$(CH_2CH_2OH)_2$		
32	Diacetyl $CH_3COCOCH_3$		

NOTES

a. Although the acid form of the compounds is given, they were employed in alkaline solution. Carboxylic acids would therefore be present as ions, or their sodium salts and enols and nitroso compounds would be present in their alkaline form.

b. Compounds 6, 11, 20, 24, 26, 27, 29, and 31 were prepared by Dr. C. F. H. Allen and his co-workers, of these Laboratories, to whom the author is greatly indebted. The remainder represent commercial samples, mostly Eastman Organic Chemicals.

6. Quinones. The resonating structure of quinone forms an interesting basis for chelate molecules, and in No. 27 may be seen to have greatly increased the potency of the weak thioglycolic acid. Compare also Nos. 11 and 30.

7. Relative potency of primary groups. The nitroso appears to be the most potent of the acidic groups, and is followed by the nitro and carboxy (see Nos. 22, 23, and 13). The phosphoric acid group has been reported on favorably and the sulfonic acid group negatively (Ref. 6).

8. Relative potency of the secondary group. The co-ordinating groups may be arranged in the following order of potency:

$$=O > OH = NH_2 > -C=C- > SH,$$

as illustrated in Compounds 9 and 15; 5, 14, and 28; 4, 12, and 25. The diazo group of No. 24 appears to be exceptionally powerful.

References

(1) Diehl, H., *Chem. Reviews*, *21*, 39 (1937).
(2) Munz, F., U. S. Patents 2,130,505 (1938) and 2,240,957 (1941).
(3) Pfeiffer, P., and Offermann, W., *Ber.*, *75B*, 1 (1942).
Pfeiffer, P., and Simons, H., *Ibid.*, *76B*, 847 (1943).
(4) Schwarzenbach, G., Kampitsch, E., and Steiner, R., *Helv. Chim. Acta*, *28*, 828 and 1133 (1945).
(5) Schwarzenbach, G., and Ackermann, H., *Ibid.*, *30*, 1798 (1947); *31*, 1029 (1948).
(6) Schwarzenbach, G., Ackermann, H., and Ruchstuhl, P., *Ibid.*, *32*, 1175 (1949).
(7) Hein, F., "Chemische Koordinations Lehre," S. Hirzel, Leipzig, 1950, p. 523.

Indicator Chart

The Eastman Indicator Chart has recently been revised and reprinted in a more convenient form. This chart, which has become very popular with those who have occasion to use or prepare indicator solutions for the determination of hydrogen ion concentrations, lists 49 acid-base indicators. The pH range in which the color change takes place is indicated by a block, and the color before and after change clearly specified. The pH ranges themselves are easily distinguishable by alternating tones in the background of the chart, making selection in any desired range much simpler. As in the previous chart, the indicators are arranged in ascending order of color change from pH 1 to pH 14. The printing is clear and legible.

In preparing an indicator for use, it is often difficult to obtain readily information regarding the recommended solvent and the suggested concentration with which the original investigator worked. Much of this information is available only in relatively obscure literature. As complete data as possible on this subject have therefore been compiled and are included on the right-hand section of the chart in the same line with each individual indicator, thus giving complete information in one convenient spot.

The entire chart and solution recommendations are printed on light cardboard measuring 11½ x 14 inches. It can be hung on a wall or filed flat. If you would like a copy, write to Eastman Organic Chemicals Department, Distillation Products Industries, Rochester 3, New York.